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⑯ Polymeric compositions useful as plant growing media additives.

⑮ Superabsorbent gel compositions useful as plant growing media additives are prepared from a copolymer of acrylamide and acrylic acid salt in a molar ratio of 70:30 to 95:5, cross-linked such that less than 30% by weight of the dry polymer is water-soluble and the gel can absorb releasably at least 15 times its own weight of water. The gel composition is therefore tailored to the needs of an agricultural/horticultural context because it has long-term stability in natural soil, low solubility that would otherwise lead to poor soil properties, and good water absorbency. Preferred gel compositions in foam form are described.

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POLYMERIC COMPOSITIONS USEFUL AS PLANT
GROWING MEDIA ADDITIVES

This invention relates to water-retentive polymeric compositions useful as plant growing media additives.

Various forms of hydrogels ("superabsorbents") have been tested as, or at least proposed for use as, growing media additives, often referred to as soil conditioners, hydromulches, and soil-water retainers. Such additives can be used to improve the properties, such as moisture retention, of conventional plant growing media, for example soil, peat, sand, loam, compost and sawdust. Alternatively, they can be used in conjunction with aqueous plant nutrient solutions to provide moisture retention and root support. An extensive review of the relevant literature is given by R A I Azzam, in Commun. Soil Science and Plant Analysis, 11(8), 767-834, (1980). It has however been difficult to achieve the preparation of a product which has an adequately high degree of moisture uptake without adversely affecting, soil properties such as aeration when the product is incorporated in soil to give it a higher water-holding capacity.

Moreover, we find that many of the available polymeric growing media additives are not sufficiently stable against chemical and/or bacterial degradation to provide long-term benefits in the practical situation, or contain too high a proportion of water-soluble material which leads to poor soil conditions. The majority of these "superabsorbent" gels were in fact developed for purposes unrelated to

agricultur , and it is not surprising that they have proved to be of relatively limited value in practical field trials.

5 One such material that has been tested as a plant growing medium additive is described in UK patent application No. 2,054,706A (Isaflex AG). This material is available commercially under the trade name "Agrohyd", and is apparently a polyacrylamide cross-linked with N,N'
10 -methylene-bisacrylamide. In our tests, this product was shown to be a substantial improvement over many previous gels, in terms of its resistance to degradation in the soil and its low solubility, but it did not seem capable of releasably absorbing moisture in quantities sufficient to
15 render it cost-effective in a practical situation.

20 By the invention, we have been able to effect a substantial improvement in the moisture-absorbing properties of polyacrylamide gels without sacrificing their useful stability in soil, thereby tailoring this particular gel type more closely to the requirements of an agricultural/horticultural context.

25 By the invention we provide a polymeric composition useful as a plant growing media additive, comprising a copolymer of acrylamide and acrylic acid salt, in a molar ratio of at least 70:30 but not greater than 95:5 cross-linked such that less than 30% of the polymeric composition (expressed by weight of the composition when dry) is water-soluble and the polymeric composition has the ability to absorb releasably at least 15 times its own weight of water. Preferably the molar ratio of acrylamide to acrylic acid salt is at least 80:20. Preferably the molar ratio is not greater than 90:10. Substituted acrylic acid salts, eg methacrylates, can be used.

By the invention we also provide a growing medium for plants, comprising a polymeric composition as defined in the preceding paragraph together with an aqueous plant nutrient solution and/or a conventional plant growing medium such as peat, loam, compost and the like.

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The gel products of the invention are capable of releasably absorbing at least 15, generally at least 20, and often at least 25, times their weight of water without significantly interfering with essential soil properties. Indeed, some gel products of the invention are capable of releasably absorbing 100 times, or more their weight of water. It will be appreciated that absorption figures for "pure" water may not be particularly significant, because the presence of minute traces of ionised solutes can markedly affect the water-absorbing properties of gel polymers. Hence it is to be expected that any gel product will actually absorb substantially less of an aqueous plant nutrient solution, and so in practice their true absorbency is lower. However, in general, the gel products of the invention are capable of releasably absorbing from 10 to 70 times their dry weight of typical aqueous plant nutrient solution. Even better water-absorbency and soil properties can often be achieved by products in which, as in a preferred embodiment, the gel composition is foamed, e.g. with a foam content equivalent to a volume increase of up to 100% or more, e.g. up to about 300%.

The polymerisation and cross-linking conditions are chosen such as would (in the absence of cross-linking) yield substantially water soluble high molecular weight polymer, but includes enough cross-linking agent to reduce the amount of water-soluble polymer (which could lead to undesirable "glue" formation on hydration) to less than 30%, and ideally less than 20%, by weight of the polymer when dry. In general, the level of cross-linking agent will not

need to be greater than 2%, and usually not greater than 1%, by weight of the total monomers. Usually the cross-linking agent will be present in an amount of at least 0.01% by weight of the total monomers. Mixtures of two or more cross-linking agents can be used if desired, and examples of suitable agents are ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate and polyethylene glycol diacrylate. Most preferred cross-linking agents are N,N'-methylene-bisacrylamide and 1,3,5-triacryloyl-hexahydro-S-triazine, and for these materials an ideal level will generally lie in the range 0.02 to 0.2% by weight of the total monomers. The proportion of soluble material in the dry polymer can conveniently be regarded for present purposes as equal to the proportion by weight which becomes non-sedimenting and ultrafiltrable after agitation of particulate (uniformly ground through 1.5mm screen) polymer in 1% NaCl solution at room temperature for 2½ hours.

It is preferred that the residual monomer in the polymer gel be not more than 1%, more preferably below 0.1%, most preferably below 0.05%. The special need for low monomer levels is due to the risk of toxicity to plants and users, and the levels which are acceptable can be checked according to the nature of the monomer with this need in mind. This can be achieved for example either by ensuring complete enough polymerisation, and/or by heating the polymer to remove residual monomer, and/or by solvent-washing. For example, residual acrylamide monomer can be removed by heating in the range 90°C-150°C for a sufficient time.

Preferably under suitable polymerisation conditions a monomer solution is polymerised by conventional UV photoinitiation using any suitable initiator, such as a benzoin alkyl ether. The total monomer level will

generally be at least about 20%, and preferably at least 25%, by weight of the solution. An upper limit will depend on the solubility of the monomers used and the viscosity of the solution, especially if a thin-film process is being performed, but generally speaking a total monomer solution concentration of up to about 55% by weight is very suitable, and an ideal concentration will generally lie in the range 30-50%. The initiator level can be varied over wide limits, eg 0.001 to 1% of the monomer, but for benzoin methyl ether, for example, about 0.1% of monomer weight is very suitable. Polymerisation conditions can be chosen to ensure autoacceleration by reaction heat to give short reaction times without causing excessive overheating.

Acrylic acid monomer units can conveniently be present as the potassium, sodium or ammonium salt or the salt of any other acceptable convenient counterion. When acrylic acid is used as a monomer it can be partly (e.g. 90%) neutralised by alkali (e.g. K_2CO_3) before the polymerisation reaction.

As mentioned above, according to a preferred feature of certain embodiments of the invention, the polymer gel is in the form of a foam. Foaming can be produced for example, by saturating the reactant mix with a dissolved gas, and ensuring that the polymerisation conditions are such that the exothermic polymerisation reaction causes a temperature rise sufficient to drive off the gas after the reaction mix has become viscous, but before gelling is complete. In this way a bubble-containing polymer gel product is formed. As an example, a CO_2 -effervescing system can be provided by saturating the reactant mix with carbon dioxide, and/or using a carbonate to neutralise an acrylic acid monomer.

Foaming can be enhanced by the inclusion of a foaming

agent (eg emulsifier, detergent) in the reactant mix prior to polymerisation, and this leads to particularly useful low-density cellular gel structures in the final product. A very wide selection of foaming agents can be used, the only significant restrictions being that the agent should not render the reactant solution opaque to UV light, should not have a harmful effect on plants if it were to be leached from the gel during use, relative cost (although the level of foaming agent employed would in any event be very low). Preferably the quantity of foaming agent added to the reactant mix should be just sufficient to give the desired degree of foaming during the polymerisation, but this quantity will clearly vary from one agent to another. Very generally, it can be said that the quantity needed will lie in the range 0.01 to 0.1 gm/litre of reactant solution. Examples of suitable foaming agent that we have found to be effective are soaps, such as sodium stearate, and emulsifiers, such as sodium stearoyl-2-lactylate. Examples of other commercially-available foaming agents are hydrolysed proteins, such as "Hyfoama DS" (Food Industries NV) and glycerol esters, such as "Emulsponge 2002" (PPF International).

Foamed products made in this way are especially advantageous as soil conditioners in that they possess a "two-stage" water-holding capacity, by virtue of water taken into cells formed by the effervescence and water physically absorbed in the microporous polymer gel structure itself. They also can show increased water uptake rate, because of their greater surface-to-volume ratio.

Particulate gel compositions according to embodiments of the invention can conveniently be made by crushing or grinding a dry polymer gel mass. The gel particles are preferably rather coarse, ie at least 0.5 mm, preferably 1 mm or more typical particle size. The gel particles are

preferably free of significant amounts of water-soluble or swellable fines which could cause formation of a gluey product on further hydration or cause potential dust problems for users. For example, one desirable composition provided by the invention comprises no more than 3% by weight of gel particles finer than 0.5mm, and substantially no gel particles smaller than 0.25mm. If necessary, fines can be removed, for example, by sieving.

The particulate gel compositions so produced can be added to soil to improve its water-holding ability, or to give water-retentive layers, mulches and packaging for use in horticulture and agriculture. It will be appreciated that the gel composition itself will not provide any nutrients to sustain plants, and it must therefore be regarded primarily as a moisture-retentive and physically-supportive material. When used in combination with an aqueous nutrient solution (containing e.g. phosphates, nitrates, plant hormones and growth regulants) and/or one or more traditional plant growing media, such as peat, loam, compost or moss, the whole provides a very suitable material in which plants can germinate, root or grow. The gel compositions of the invention are particularly well suited for use in the potting or rooting of immature plants in a nursery prior to transfer to field or plantation conditions, and as such can be mixed in minor proportion with a rooting (root-holding) medium such as wood fibre, peat, forest bark, straw, loam, or particulate plastics material.

Alternatively, the gel product of the invention can be manufactured and used in shaped form, such as sheets to provide water-retentive layers in soil or linings for plant pots, seed trays and other receptacles. Hollow or recessed "cubes" or other three-dimensional shapes can be used, to provide ideal miniature environments in which seeds can be sown or in which seedlings can be grown or transplanted.

The proportion of gel product used can be varied according to the situation. When employed as a soil additive, levels of inclusion as low as 0.5-1% by weight of gel/volume of growing medium can lead to significant soil improvements. In this context generally only a few percent of the gel are required, and levels in excess of 4% by weight may not be considered economic. However, in a small-scale potting or rooting procedure the gel can be used simply in conjunction with an aqueous nutrient solution and the gel therefore represents 100% of the solids present, although in this context it will generally be sensible on cost grounds to mix the gel with one or more cheaper supportive fillers such as sawdust, straw or sand.

The invention is illustrated without limiting its scope, by the several features of the following Examples.

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Example 1

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Acrylic acid (48.7g) containing benzoin methyl ether (0.24g) was completely neutralised with potassium carbonate (47.3g) as a solution in water (120 mls). To this mixture acrylamide (192g) and methylenebisacrylamide (0.24g), as a solution in water (240 mls), was added. The solution was shielded from light as much as possible and was purged with nitrogen for 10 minutes.

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The reactant mix was poured into pyrex glass dishes so as to give a film thickness of approximately 7.5mm and irradiated with long wave length ultra-violet light (2 x 40 watt tubes peaking at 365 nm giving an incident light intensity of 4000 uW/cm²). The solution rapidly gelled to a give a non-foamed rubbery polymer accompanied by a rapid temperature rise, typically from 20°C to 100°C in 1½ minutes. The total irradiation time was typically 5-10 minutes.

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The rubbery polymer film was removed from the glass dishes and dried and crushed to give a particulate product. Fines were removed by sieving to reduce the likelihood of "glue" formation during use. The product was capable of absorbing 43 times its dry weight of a conventional phosphate-containing plant nutrient solution. The dry product contained just under 20% by weight of water-soluble material.

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To a solution of acrylamide (1800g) in water (1950 mls) was added potassium carbonate (195.5g) in water (500 mls). To this mixture, acrylic acid (204 g) containing benzoin methyl ether (2 g) and methylenebisacrylamide (1 g) was slowly added with stirring to complete the neutralisation reaction. The solution was shielded from light as much as possible and purged with nitrogen to flush out carbon dioxide from the carbonate neutralisation.

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The reactant mix was then pumped to give a film thickness of 5-9 mm on a moving conveyor, which was shaped by the action of folding cheeks and a suction box to give a trough shape configuration which contained the liquid reactants. The conveyor then carried the solution through a nitrogen-filled cavity where it was irradiated with long wavelength UV light (2 x 40 watt tubes peaking at 365 nm, giving $3500 \pm 200 \text{ } \mu\text{W/cm}^2$ incident light intensity). Polymerisation was rapid and accompanied by a rapid temperature rise, reaching in excess of 100°C after 2-3 minutes. Some large bubbles were formed in the polymer film due to the boiling point of water being exceeded but the final material was not foamed. The total irradiation time was in excess of 20 minutes.

The rubbery polymer film was dried and crushed. The

dry product could absorb 31 times its own weight of a conventional phosphate-containing plant nutrient solution. The dry product contained 9% by weight of water-soluble material.

5 Example 3

10 The procedure of Example 2 was repeated, using identical materials, quantities and reaction conditions, except that a dispersion of "Emulsponge 2002" (a commercially-available foaming agent obtained from PPF International) was added to the reactant mix and the nitrogen purging was omitted. The dispersion contained 1 g of foaming agent in 50 ml water.

15 During the polymerisation reaction there was a sudden and large increase in the volume of the polymer, due both to the boiling of the aqueous mixture and to the release of carbon dioxide from solution. The formation of a foamed gel was greatly enhanced by the addition of the foaming agent.

20 The foamed polymer film was dried and crushed. The dry material was capable of absorbing 39 times its own weight of a conventional aqueous phosphate-containing plant nutrient solution, and had a water-soluble material content of 11% by weight.

25 All of the dry particulate polymers of Examples 1 to 3 were free-flowing light-coloured materials. When blended with soil, damp compost, and other conventional plant growing media, and hydrated, they provided very good moisture retention and remained stable in a natural environment for many weeks. They showed little tendency to "glue" the soil particles together, due to their low content of water-soluble material.

Example 4Stability of acrylamide/acrylic acid salt backbones

5 To study the inherent stability of hydrated polymer
backbones, their molecular weight as a function of time in
solution was examined for a range of water-soluble
acrylamide/sodium acrylate copolymers. The weight average
molecular weights (M_w) were determined by low angle laser
light scattering using 0.2M aqueous sodium chloride as
solvent. The samples required dialysis against this
10 solvent for at least seven days before the
characterisation.

The molecular weights as a function of time are shown
in Table 1. The figures in brackets give relative
molecular weights.

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Table 1
Weight Average Molecular weights (x10⁻⁶)

Copolymer molar ratio, poly (acrylamide:sodium acrylate)						
Age (days)	90:10	85:15	70:30	60:40	50:50	40:60
7	6.5(1.0)	—	—	—	—	—
9	—	10.9(1.0)	8.2(1.0)	4.4(1.0)	2.6(1.0)	—
14	8.0(1.0)	6.6(1.02)	—	—	—	—
21	—	—	8.2(0.75)	3.5(0.43)	2.0(0.45)	0.95(0.37)
28	—	6.9(1.06)	—	—	—	—
29	8.6(1.08)	—	—	—	—	—
30	—	—	6.6(0.61)	2.3(0.28)	0.98(0.22)	0.51(0.20)
41	—	—	6.1(0.56)	1.9(0.23)	0.76(0.17)	0.44(0.17)
42	8.3(1.04)	6.3(0.97)	—	—	—	—
83	7.8(0.98)	—	—	—	—	—

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It can be seen that polymers containing 40 mol% or more of sodium acrylate have poor stability in solution as shown by a rapid decrease in molecular weight with time. Copolymers containing 30 mol% or less of sodium acrylate show greatly increased stability.

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Example 5

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A range of polymer gels containing different molar ratios of acrylamide:potassium acrylate were prepared as follows and assessed for their relative abilities to absorb plant nutrient solution and for their relative solubilities.

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Each gel was prepared by dissolving 10 mgs N,N'-methylene-bisacrylamide and a quantity of acrylamide in water, adding an aqueous solution of potassium carbonate, and then adding the whole mixture to a solution of 10mgs benzoin methyl ether in acrylic acid. The reactant mix was shielded from the light, and purged with nitrogen for 10 minutes. Polymerisation was effected as in Example 1.

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Each polymerised product was dried overnight at 90°C, milled to pass a 1.5 mm screen.

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The actual quantities and proportions of the materials used are set out in Table 2 below, together with the relevant properties of "retention" (ie gm of a conventional aqueous phosphate-containing plant nutrient solution absorbed per gm of the dry polymer material) and "initial solubility" (ie percentage by weight of the dry polymer material soluble in water as assessed using the test procedure hereinbefore described)

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The results show that retention improves with increasing proportion of acrylic acid salt in the polymer

backbone, but at the expense of a greater % of soluble, potentially gluey, material in the dry polymer. These findings should be read in conjunction with the stability data given in Table 1 of Example 4.

5 Example 6

This Example shows in Table 3 below the properties of two commercially-available "superabsorbent" polyacrylate materials, recommended for use in agriculture/horticulture, compared with a material in accordance with the invention, prepared as per Example 2 above.

10

The commercially-available materials are:

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"Viterra 2" (ex Nepera Chemical Co), which we believe to be a very lightly cross-linked polyacrylamide/potassium acrylate copolymer, having an acrylamide:acrylate molar ratio of about 70:30.

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"Agrohyd G12H" (ex Isaflex AG), which we believe to be a very heavily cross-linked polyacrylamide containing a low proportion (probably not more than 5 molar %) of acrylate groups due to hydrolysis of the acrylamide.

Table 2

Acrylamide: K ⁺ acrylate	gm acrylamide +	gm K ₂ CO ₃ + mls water	gm acrylic acid	Retention	Initial solubility
50:50	5	8	4.93	7	5.08
60:40	6	8	3.94	7	4.06
70:30	7	9	2.96	6	3.05
80:20	8	10	1.97	5	2.03
90:10	9	10	0.99	5	1.02
100:00	10	15	-	-	-
				103	24.0
				97	19.5
				84	15.5
				71	12.4
				45	7.9
				6.9	3.5

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Table 3

	<u>"Viterra 2"</u>	<u>Product of Example 2</u>	<u>"Agrohyd G12H"</u>
5	Distilled water absorbency (gm/gm dry product)	240	50
10	Nutrient solution absorbency (gm/gm dry product)	150	31
15	Soluble fraction (% by weight)	50	9

All three materials possess good stability against degradation in natural soil.

However, "Viterra 2" has a very high content of water-soluble material which leads to poor soil properties, especially aeration, although it possesses an outstanding ability to absorb moisture. We believe this deficiency is due to inadequate cross-linking.

On the other hand, "Agrohyd G12H" shows a very low level of undesirable water-soluble material, probably due to the heavy cross-linking, but its ability to absorb moisture is also low.

The product of the invention provides an effective balance of properties between the two extremes exemplified by these commercially-available products.

* * * * *

CLAIMS

1. A polymeric composition useful as a plant growing media additive, comprising a copolymer of acrylamide and (meth)acrylic acid salt in a molar ratio of at least 70:30 but not greater than 95:5 cross-linked such that less than 30% of the polymeric composition (expressed by weight of the composition when dry) is water soluble and the polymeric composition has the ability to absorb releasably at least 15 times its own weight of water.
2. A composition according to Claim 1, wherein the molar ratio of acrylamide to (meth)acrylic acid salt is at least 80:20.
3. A composition according to Claim 1 or Claim 2, wherein the molar ratio of acrylamide to (meth)acrylic acid salt is not greater than 90:10.
4. A composition according to any one of the preceding claims, wherein less than 20% of the polymeric composition (expressed by weight of the composition when dry) is water soluble.
5. A composition according to any one of the preceding claims, capable of releasably absorbing at least 20 times its weight of water.
6. A growing medium for plants, comprising a polymeric composition as claimed in any one of the preceding claims together with an aqueous plant nutrient solution and/or a conventional plant growing medium such as soil, peat, loam or compost.

7. A process for the preparation of a polymeric composition useful as a plant growing medium additive, in which process a mixture of acrylamide and (meth)acrylic acid salt in a molar ratio of at least 70:30 but not greater than 95:5 is copolymerised in the presence of a cross-linking agent in an amount sufficient to ensure that less than 30% of the resulting polymeric composition (expressed by weight of the composition when dry) is water soluble while enabling the polymeric composition to absorb releasably at least 15 times its own weight of water.

8. A process according to Claim 7, wherein the molar ratio of acrylamide to (meth)acrylic acid salt is at least 80:20.

9. A process according to Claim 7 or Claim 8, wherein the molar ratio of acrylamide to (meth)acrylic acid salt is not greater than 90:10.

10. A process according to any one of Claims 7 to 9, wherein the cross-linking agent is present in an amount sufficient to ensure that less than 20% of the resulting polymeric composition (expressed by weight of the polymeric composition when dry) is water soluble.

11. A process according to any one of claims 7 to 10, wherein the cross-linking agent is N,N'-methylene-bisacryl amide and/or 1,3,5-triacryloyl-hexahydro-S-triazine.

12. A process according to any one of Claims 7 to 11, wherein the quantity of cross-linking agent present in the reactant mix is from 0.02 to 0.2% by weight of the total monomers.

13. A process according to any one of claims 7 to 12, wherein the polymer is produced in foam form by causing a gas to be driven from the reaction mix after it has become viscous but before gelling is complete.

14. A process according to Claim 13, in which the gas is carbon dioxide.

15. A process according to Claim 13 or Claim 14, in which foaming is enhanced by the presence of a foaming agent.

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